

(12) **UK Patent Application** (19) **GB** (11) **2 148 917 A**

(43) Application published 5 Jun 1985

(21) Application No **8328546**

(22) Date of filing **26 Oct 1983**

(71) Applicant
**Kodak Limited (United Kingdom),
Kodak House, Station Road, Hemel Hempstead,
Hertfordshire**

(72) Inventor
Paul William Law

(74) Agent and/or Address for Service
**P A C Baron, I E Davis, R F Nunney,
Kodak Limited, Patent Department, Headstone Drive,
Harrow, Middlesex HA1 4TY**

(51) INT CL⁴
**C09B 29/033 29/44 D06P 1/18 1/39 // C07D
215/02**

(52) Domestic classification
**C4P 126 1D3 1F1 1F2 1F4 1F5 1F6 1G 1H2 9A3A1
C2C 1543 213 246 247 250 251 25Y 305 30Y 776
AA ZH
U1S 1347 1399 1565 C2C C4P**

(56) Documents cited
None

(58) Field of search
C4P

(54) **Disperse and acid azo dyes from 2-aminothiophene and 1,2-dihydroquinoline couplers**

(57) New dyes of formula (I) give blue to green shades on polyamide fibres:



wherein C¹ is an optionally substituted 1,2-dihydroquinoline coupler and each R is a substituent.

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SPECIFICATION

Disperse and acid azo dyes from 2-aminothiophene and 1,2-dihydroquinoline couplers

- 5 This invention concerns disperse and acid dyes particularly suited for the dyeing of polyamide fibres. 5

The dyes of the present invention are made by coupling a diazotized 2-aminothiophene with a 1,2-dihydroquinoline coupler and so have the general formula:



- 15 wherein C¹ is an unsubstituted or substituted 1,2-dihydroquinoline moiety and each R is a 15
 halogen atom or an alkyl, alkoxy, alkanoyl, nitro, alkylsulfonyl, SO₂NH₂, SO₂NHalkyl, SO₂N(al-
 kyl)₂, SO₃M, alkyl-SO₃M, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxy-carbonyl, alkanoyloxy, SO₃al-
 kyl, arylsulfonyl, acylamido, aryl, aroyl, aryloxy, arylthio, alkenyl of 2-8 carbon atoms,
 20 alkenylthio of 2-8 carbon atoms, cyclohexyl, cyclohexylthio, cyclohexylsulfonyl, cyano, thiocy- 20
 ano, SO₃C₆H₅, or alkylthio group, M being hydrogen, sodium, potassium, ammonium, Ca/2,
 Zn/2 or a colourless cation of a primary, secondary or tertiary aliphatic or aromatic amine. Any
 alkyl, alkenyl or cyclic moiety in a group R may be substituted as specified below.

Preferred dyes of the invention are of the general formula:



- 35 wherein R₁ is H or an alkyl, aryl, or cyclohexyl group; R₂ and R₃ are each independently selected 35
 from H and alkyl; R₄ is H, alkyl or alkyl-SO₃M; and R₅ is H, alkyl, alkoxy, alkenyl of 2-8
 carbons, halogen, acylamido, alkylthio or formamido, wherein any alkyl moiety may be
 substituted with 1-3 of -OH, halogen, -CN, alkoxy, SO₃M, alkylthio, alkanyoyl, alkanoyloxy,
 or alkoxy-carbonyl; and wherein any alkyl, alkenyl and cyclic moieties in the defined ring
 40 substituents of the thiophene or in R₁ may bear up to three substituents different from the 40
 moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, aryloxy, cyclohexyl, furyl,
 (C₄H₉O), aroyloxy, alkoxy-carbonyl, alkanoyloxy, SO₂NH₂, SO₃M, alkyl-SO₃M, SO₂NHaryl, SO₂N-
 Halkyl, SO₂N(alkyl)₂, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido
 (C₄H₄O₂N), glutarimido (C₅H₆O₂N), aroyl, phthalimido (C₈H₄O₂N), 1-(2-pyrrolidono) (C₄H₆OH),
 45 cyclohexoxy, cyano, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxy-alkoxy, alkylthio, halogen, arylthio, 45
 alkylsulfonyl, arylsulfonyl, alkoxy-carbonylamino, -NO₂ and aryloxy.

The various alkyl and alkylene moieties in, for example, alkoxy, alkanoyl and the like within
 the above definitions of R₁ - R₅, and the thiophene ring substituents preferably have 1-6
 carbons, and they and the alkenyl groups are straight or branched chain.

- 50 Preferred dyes of the present invention are where the thiophene ring substituents are selected 50
 from alkyl, nitro, CONH₂, CONHalkyl, CON(alkyl)₂, alkyl-SO₃M, SO₂-alkyl, SO₂-aryl, alkoxy-carbo-
 nyl, CONHalkyl-OH, SO₂NH₂, SO₂NHalkyl, and SO₂N-(alkyl)₂.

The dyes of this invention impart blue to green shades on fibers, particularly polyamides,
 exhibiting improvements in fastness to one or more of light, ozone, perspiration, oxides of
 55 nitrogen, washing, sublimation and crocking, and show improvements in one or more of 55
 leveling, transfer, pH stability, exhaustion, build and are non-red flaring.

The diazo components used in this invention are prepared according to procedures well
 known to the art.

- The preparation of the sulfonated 1,2-dihydroquinoline is given in German Offen. 3,005,874
 60 (C.A. 94, 15593K, 1981) and comprises sulfonating the 4-alkyl-1,2-dihydroquinoline with 60
 H₂SO₄, ClSO₃H, and/or SO₃ and converting, if desired, the acid group to its salt in known
 manner. The present disperse dyes may be applied to polyamide fibers by conventional dyeing
 procedures, e.g., dispersed in a lignin sulfonate and dyed at 98°C. on nylon fabric for one hour
 from an aqueous bath.

- 65 The acid dyes of the invention may be applied to polyamide fiber by the following method: 65

The test dye, as a mixture with a sulphate such as ammonium sulfate, is pasted with boiling water and then made up to a known volume with water to give a weight ratio of water to dye of 30:1. Four percent on weight of fiber (owf) of a lignin sulphonate leveling agent is added, followed by ammonium acetate (about 3.0% owf) to adjust the pH to 6. The initial dyeing temperature is 40°C. which is raised to the final dyeing temperature of 98°C. for 30 minutes. The dye bath is held at 98°C. for 60 minutes, then cooled, and the test fabric given a warm water rinse and air drying.

The following examples illustrate procedures which are generally applicable for preparation of the present couplers and dyes. The examples are included merely for purposes of illustration and are not intended to limit the scope of the invention.

EXAMPLE 1

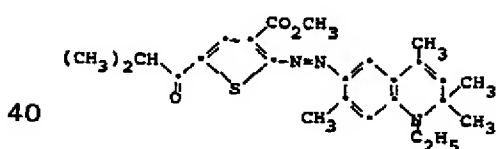
(a)—Preparation of 1,2-Dihydro-2,2,4,7-Tetramethylquinoline

Meta-toluidine (535 g.) and iodine (6 g.) are charged to a 2 liter, 3 neck, round bottom flask. The reaction is heated to 155°C. and about 3500 g. of acetone is added at 155–160°C. beneath the surface over a 12 hour period. A mixture of acetone and water distills off during the addition. The reaction mixture is heated one-half hour at 160°C. and then distilled to leave about 690 g. of 1,2-dihydro-2,2,4,7-tetramethylquinoline boiling at 107–111°C. at 0.55 mm., a 74% yield. Where it is desired, for example, to obtain the >N-ethyl derivative, the above product can be ethylated with triethylphosphate in the presence of ethyl iodide.

(b)—Diazotization and Coupling

2-Amino-3-carbomethoxy-5-isobuteryl thiophene (11.35 g., 0.05 mole) was added to 60% aqueous acetic acid (125.0 cm³), with stirring, followed by concentrated sulphuric acid (10.0 cm³). The mixture was cooled to 0°C. Sodium nitrite (3.59 g., 0.05 mole) was added to concentrated sulphuric acid (46.0 cc.) and the solution heated to 70°C., for 5 minutes. On cooling to 0°C. the solution was added slowly to the above amine mixture, at 0–5°C. After stirring at 0–5°C. for a further one hour, the diazo solution was added to 1-ethyl-2,2,4,7-tetramethyl-1,2-dihydro-quinoline (10.75 g., 0.05 mole) in 50% aqueous ethanol (54.0 cc.) containing sodium acetate (2.05 g), at <5°C. After stirring at 0–5°C. for one hour the dye was warmed to room temperature and precipitated by adding to cold water. The product was filtered and washed well with water to yield 11.32 g. (50%) of the final dye product, I, of the formula

35



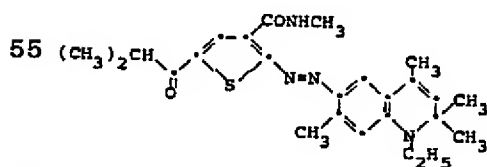
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(I)

EXAMPLE 2

Dye I (4.53 g., 0.01 mole) was dissolved in 23 cc. of dimethylformamide and 10 cc. of 40% aqueous methylamine was added and stirred at room temperature for 12 hours. The mixture was poured into 150 cc. of water and the precipitated product filtered and washed well with water to yield 4.06 g. (90%) of the final dye product, II, of the formula

50



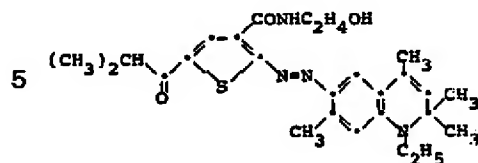
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(II)

EXAMPLE 3

Using the above procedure in Example 2, Dye III of the formula below was prepared from ethanolamine.

65

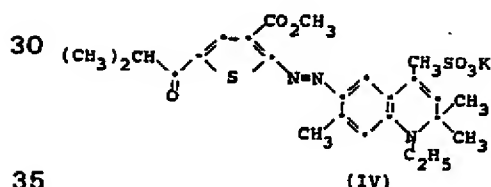


(III)

EXAMPLE 4

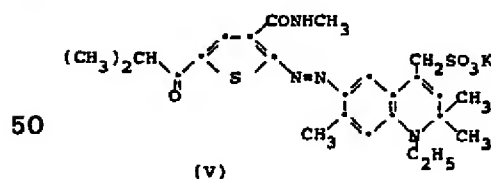
15 2-Amino-3-carbomethoxy-5-isobutyrylthiophene (2.27 g., 0.01 mole) was added to 60% aqueous acetic acid (25.0 cc.), with stirring, followed by concentrated sulphuric acid (2.0 cc.). The mixture was cooled to 0°C. Sodium nitrite (0.72 g., 0.0104 mole) was added to concentrated sulphuric acid (9.2 cc.) and the solution heated to 70°C., for 5 minutes. On cooling to 0°C. the solution was added slowly to the above amine mixture, at 0-5°C. After stirring at 20 0-5°C. for a further 1 hour, the diazo solution was added to the potassium salt of 1-ethyl-2,2,7-trimethyl-1,2-dihydroquinolin-4-yl-methyl sulphonic acid (3.33 g., 0.01 mole), in water (11.0 cc.) at <5°C.

After stirring at 0-5°C. for 1 hour the dye was warmed to room temperature and precipitated by adding to saturated potassium chloride solution. The product was filtered and washed with 25 diethyl ether, to yield 3.70 g. (64.8%) of the final dye product, IV.



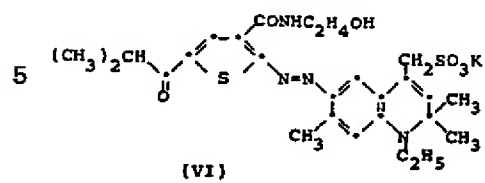
EXAMPLE 5

40 Dye IV (5.71 g., 0.01 mole) was dissolved in a 30% ethanolic solution of methylamine (28.5 cc.) and stirred at room temperature for 2 hours. The excess ethanol and methylamine were evaporated, yielding 5.70 g. (100%) of the final dye product, V.



EXAMPLE 6

55 Using the above procedure, in Example 5, Dye VI was prepared from ethanolamine, resulting in a yield of 6.0 g. (100%).



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The following table gives additional exemplary dyes of the present invention.

3-CH ₃	H	CH ₃	CH ₂ CH ₂ OH
3-CONHCH ₃	OCH ₃	C ₂ H ₅	CH ₂ CH ₂ SO ₂ N(C ₂ H ₅) ₂
5-CON(C ₂ H ₅) ₂	NHCHO	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
5-CH ₂ SO ₂ NHCH ₃	NHCOCH ₂ OCCH ₃	CH ₃	CH ₂ CN
5-C ₆ H ₅	NHCOCH ₂ CH ₃	C ₃ H _{7-n}	CH ₂ CONH ₂
5-CH ₃	NHCOCH ₂ Cl	CH ₃	CH ₂ CONHCH ₃
5-CH ₂ NHCOOCH ₃	NHCOCH ₆ H ₅	CH ₃	CH ₂ CON(C ₂ H ₅) ₂
4-SCN	NHCOCH ₂ H ₅	C ₄ H _{9-n}	CH ₂ NHCOCH ₃
4-CH ₂ NHCONHCH ₃	NHCOCH ₆ H ₁₁	CH ₃	CH ₂ NHCOOCH ₃
4-OCH ₃	H	CH ₃	CH ₂ OOCCH ₃
3-Br	CH ₂ SCCH ₃	H	CH(C ₄ H ₆ ON)
3-CF ₃	CH ₂ CH=CH ₂	H	CH ₂ CH ₂ COOCH ₃
3-OCH ₂ CH ₃	Br	H	CH ₂ CH ₂ COOCH ₃
3-SCH ₃	I	H	H
3-SCN	F	H	C ₂ H ₄ SC ₂ H ₅
3-SO ₂ NH ₂	SCCH ₃	H	C ₃ H _{7-n}

3-SO ₂ NHC ₄ H ₉ -n	CH ₂ OOCCH ₃	H	CH ₃	CH ₃	C ₄ H ₉ -n
3-SO ₂ N(CH ₃) ₂	OCH ₃	H	CH ₃	CH ₃	C ₂ H ₄ C ₆ H ₅
3-SO ₃ C ₆ H ₅	CH ₃	H	CH ₃	CH ₃	C ₂ H ₄ C ₆ H ₁₀ -P-SO ₃ K
4-CN	H	H	H	H	CH ₂ Cl
4-CONH ₂	CH ₂ CH ₂ COOCH ₃	H	CH ₃	CH ₃	C ₆ H ₄ -P-OCH ₃
4-COOCH ₂ SO ₃ K	CH ₂ CH(OH)CH ₂ OH	H	CH ₃	CH ₃	C ₆ H ₁₀ -P-OH
4-COOCH ₃	CF ₃	H	CH ₃	CH ₃	C ₂ H ₅
4-COC ₆ H ₅	CF ₃	H	CH ₃	CH ₃	CH ₂ CHSC ₆ H ₅
4-Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₂ CHSO ₂ CH ₃
4,5-di-Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₂ CHSO ₂ C ₆ H ₅
4-Br	CH ₂ CH(Cl)CH ₂ Cl	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₂ CHOC ₂ H ₄ OC ₂ H ₅
4-CF ₃	CH ₂ CH(OCH ₃)CH ₂ OCH ₃	CH ₃	CH ₃	CH ₃	CH ₂ (C ₈ H ₄ O ₂ N)
5-NHCOCH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CONH ₂
5-SO ₂ CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	CH ₂ (C ₄ H ₄ O ₂ N)
5-CH ₂ SO ₂ NHC ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CON(C ₂ H ₅) ₂
5-CH ₂ SO ₂ N(C ₂ H ₅) ₂	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ NHCONHCH ₃
5-SO ₂ NHC ₂ H ₅	H	CH ₃	CH ₃	CH ₃	CH ₂ NHSO ₂ CH ₂ NO ₂

5-CH ₂ CH ₂ NHCOCH ₂ Cl	H	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ OOCCH ₃
5-CH ₂ NHSO ₂ CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ NH ₄	CH ₂ (C ₄ H ₉ O)
5-CH ₂ CH ₂ CH ₂ (C ₄ H ₉ ON)	CH ₂ CH ₂ OH	CH ₃	CH ₃	CH ₃	H	CH ₂ CH ₂ COOCH ₃
None	CH ₂ Cl	CH ₃	CH ₃	CH ₃	H	CH ₂ CH ₂ OOCCH ₂ H ₅
3-CH ₂ CH ₂ CN	OCH ₂ Cl	CH ₃	CH ₃	CH ₃	C ₃ H ₇ -n	H
3-NHCOCH ₂ CN	OCH ₃	CH ₃	CH ₃	CH ₃	C ₃ H ₇ -n	C ₂ H ₅
3-CH ₂ (C ₄ H ₉ O ₂ N)	OCH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₃ H ₇ -n
3-CH ₂ (C ₅ H ₆ O ₂ N)	CH ₂ CH ₂ CN	CH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₄ H ₉ -n
3-CH ₂ CH ₂ (C ₈ H ₄ O ₂ N)	Cl	CH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅
3-CH ₂ CONH ₂	Cl	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
3-CH ₂ CONHCH ₃	H	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
3-CH ₂ CH ₂ OCH ₂ CH ₂ OC ₂ H ₅	OCH ₃	CH ₃	CH ₃	CH ₃	CH ₃	C ₆ H ₄ -P-CH ₃
3-COOCH ₂ CH ₂ OCH ₃	NHCHO	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ NH ₄	C ₆ H ₁₁
3-CH ₂ CH ₂ SCCH ₃	NHCOCH ₂ OCH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ OC ₆ H ₅
3-CH ₂ CH ₂ CH ₂ Cl	NHCOCH ₂ CH ₃	H	H	H	H	CH ₂ CH ₂ OH
3-CH ₂ SC ₆ H ₅	NHCOCH ₂ Cl	H	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH
5-CH ₂ SO ₂ CH ₃	NHCOCH ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH

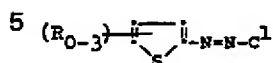
4-CH ₂ SO ₂ C ₆ H ₅	NHCO ₂ C ₂ H ₅	CH ₃	CH ₃	CH ₂ SO ₃ Na	CH ₂ CH ₂ OCH ₂ CH ₂ NHCOCH ₃
4-CH ₂ CH(OH)CH ₂ OH	NHCO ₂ C ₆ H ₁₁	H	CH(CH ₃) ₂	CH ₃	CH ₂ CN
4-CH ₂ CH(OH)CH=CH ₂	H	H	CH ₃	CH ₃	CH ₂ CONH ₂
4-C ₆ H ₄ -p-OH	CH ₂ SCH ₃	H	CH ₃	H	CH ₂ CONHCH ₃
5-C ₆ H ₄ -p-C ₂ H ₅	CH ₂ CH=CH ₂	H	CH ₃	H	CH ₂ CON(C ₂ H ₅) ₂
5-C ₆ H ₄ -p-OC ₆ H ₅	Br	H	CH ₃	CH ₂ SO ₃ K	CH ₂ NHCOCH ₃
5-C ₆ H ₄ -p-C ₆ H ₁₁	I	H	CH ₃	CH ₃	CH ₂ NHCOOCH ₃
5-C ₆ H ₄ -p-(C ₄ H ₉ O)	F	H	CH ₃	CH ₃	CH ₂ OOCCH ₃
5-C ₆ H ₄ -p-OCC ₆ H ₅	SCH ₃	H	CH ₃	CH ₃	CH ₂ (C ₄ H ₉ ON)
5-C ₆ H ₄ -o-COOCH ₃	CH ₂ OOCCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₂ CH ₂ COCH ₃
5-C ₆ H ₄ -m-SO ₂ NH ₂	OCH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ COOCH ₃
5-C ₆ H ₄ -p-CONH ₂	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	H
5-C ₆ H ₄ -p-NHCONHCH ₃	H	C ₃ H ₇ -n	C ₃ H ₇ -n	H	C ₂ H ₅
5-C ₆ H ₄ -m-(C ₈ H ₄ O ₂ N)	CH ₂ CH ₂ COOCH ₃	CH ₃	CH ₃	H	C ₃ H ₇ -n
5-C ₆ H ₃ -o, p-di-CN	CH ₂ CH(OH)CH ₂ OH	CH ₃	CH ₃	H	C ₄ H ₉ -n
3-C ₆ H ₂ -o, m, p-tri-Cl	CF ₃	C ₄ H ₉ -n	C ₄ H ₉ -n	H	C ₂ H ₅
3-C ₆ H ₄ -p-OCH ₂ CH ₂ OCH ₃	CF ₃	CH ₃	CH ₃	H	C ₂ H ₅

3-C ₆ H ₄ -p-SC ₆ H ₅	H	CH ₃	CH ₃	H	CH ₃
5-C ₆ H ₄ -p-SO ₂ CH ₂ SO ₃ K	H	H	CH ₃	H	C ₆ H ₅
5-C ₆ H ₄ -p-SO ₂ C ₆ H ₅	CH ₂ CH(Cl)CH ₂ Cl	H	H	H	C ₆ H ₁₁
5-C ₆ H ₁₀ -p-Cl	CH ₂ CH(OCH ₃)CH ₂ OCH ₃	H	CH ₃	CH ₂ SO ₃ K	C ₂ H ₅
3-C ₆ H ₉ -o,p-di-OH	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
3-C ₆ H ₁₀ -p-CH ₃	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
3-C ₆ H ₁₀ -p-OC ₂ H ₅	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
3-CH ₂ CH ₂ SO ₂ NHC ₆ H ₅	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
3-C ₆ H ₄ -p-SO ₂ NHC ₆ H ₅	H	H	CH ₃	CH ₃	CH ₂ CN
3-CH ₂ CH ₂ OCH ₂ C ₆ H ₅	H	H	CH ₃	CH ₂ SO ₃ NH(CH ₃) ₃	CH ₂ CONH ₂
5-C ₆ H ₁₁	H	H	CH ₃	CH ₃	C ₆ H ₄ -p-(C ₄ H ₄ O ₂ N)
5-SC ₆ H ₅	H	H	CH ₃	CH ₃	C ₆ H ₁₀ -p-OCH ₃
4-OOCCH ₃	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	C ₆ H ₄ -p-Cl
4-SO ₃ -CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ (C ₅ H ₆ O ₂ N)
5-SO ₂ C ₆ H ₄ -p-SO ₃ K	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
5-SC ₆ H ₁₁	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH
5-SO ₂ C ₆ H ₁₁	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ CN

4-SO ₃ K	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ Br
3-CON(CH ₃) ₂ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
3-CON(C ₂ H ₅) ₂ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
3-SO ₂ C ₆ H ₅ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
3-SO ₂ CH ₃ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
3-CONHCH ₃ , 5-SO ₂ NH ₂	H	CH ₃	CH ₃	CH ₃	C ₂ H ₅
3-CN, 5-SO ₂ N(C ₂ H ₅) ₂	H	CH ₃	CH ₃	CH ₃	C ₂ H ₅
3-CON(CH ₃) ₂ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	C ₂ H ₅
3-CON(C ₂ H ₅) ₂ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	C ₂ H ₅
3-SO ₂ C ₆ H ₅ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	C ₂ H ₅
3-SO ₂ CH ₃ , 5-COCH(CH ₃) ₂	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	C ₂ H ₅
3-CONHCH ₃ , 5-SO ₂ NH ₂	H	CH ₃	CH ₃	CH ₂ SO ₃ K	C ₂ H ₅
3-CN, 5-SO ₂ N(C ₂ H ₅) ₂	H	CH ₃	CH ₃	CH ₂ SO ₃ K	C ₂ H ₅

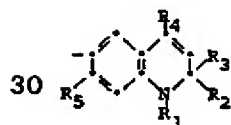
CLAIMS

1. A dye of the formula



wherein C¹ is a 1,2-dihydroquinoline moiety which is unsubstituted or substituted, and wherein each R is alkyl, alkoxy, alkanoyl, —NO₂, halogen, alkylsulfonyl, SO₂NH₂, SO₂NHalkyl, SO₂N(alkyl)₂, SO₃M, alkyl-SO₃M, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxycarbonyl, alkanoyloxy, SO₃-alkyl, arylsulfonyl, acylamido, aryl, aroyl, aryloxy, arylthio, alkenyl of 2–8 carbons, alkenylthio, cyclohexylthio, SO₃C₆H₅, cyano, thiocyno, cyclohexyl-sulfonyl, alkylthio, or cyclohexyl, any alkyl, alkenyl or cyclic moiety in a substituent R possibly bearing up to three substituents different from the moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, aryloxy, cyclohexyl, furyl (C₄H₃O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO₂NH₂, SO₃M, alkyl-SO₃M, SO₂NH-aryl, SO₂NHalkyl, SO₂N(alkyl)₂, NHCOO-alkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido (C₄H₄O₂N), glutarimido (C₅H₆O₂N), aroyl, phthalimido (C₈H₄O₂N), 1-(2-pyrrolidino) (C₄H₆OH), cyano, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxyalkoxy, alkylthio, halogen, cyclohexoxy, arylthio, alkylsulfonyl, arylsulfonyl, alkoxycarbonylamino, —NO₂ and aryloxy, and M being selected from H, Na, K, NH₄, Ca/2, Zn/2 and colorless cations of primary, secondary and tertiary aliphatic and aryl amines.

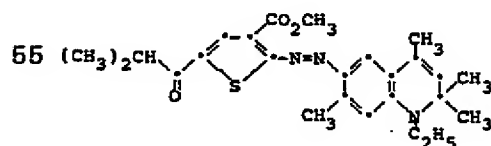
2. A dye according to Claim 1 wherein the coupler C has the formula



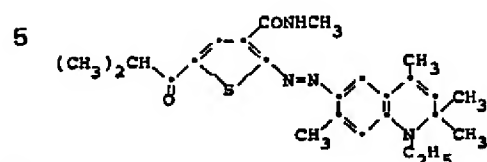
wherein R₁ is H or a group selected from alkyl, aryl, and cyclohexyl; R₂ and R₃ are each independently selected from H and alkyl; R₄ is H, alkyl or alkyl-SO₃M, and R₅ is selected from H, alkyl, alkoxy, alkenyl of 2–8 carbons, halogen, acylamido, alkylthio and formamido, wherein any alkyl moiety may be substituted with 1–3 of —OH, halogen, —CN, —SO₃M, alkoxy, alkylthio, alkanoyl, alkanoyloxy, or alkoxycarbonyl; and wherein any alkyl, alkenyl and cyclic moieties in the defined ring substituents of the thiophene and of R₁ may bear up to three substituents different from the moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, aryloxy, cyclohexyl, furyl (C₄H₃O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO₂NH₂, SO₂NH-aryl, SO₂NHalkyl, SO₃M, SO₂N(alkyl)₂, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido (C₄H₄O₂N), glutarimido (C₅H₆O₂N), aroyl, phthalimido (C₈H₄O₂N), 1-(2-pyrrolidino) (C₄H₆OH), cyano, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxyalkoxy, alkylthio, halogen, cyclohexoxy, arylthio, alkylsulfonyl, arylsulfonyl, alkoxycarbonylamino, —NO₂ and aryloxy.

3. A dye according to claim 2 wherein the thiophene ring substituents are selected from alkyl, nitro, CONH₂, CONHalkyl, CON(alkyl)₂, CN, SO₂alkyl, alkyl-SO₃M, SO₂aryl, alkoxycarbonyl, CONHalkyl-OH, SO₂NH₂, SO₂NHalkyl, and SO₂N(alkyl)₂.

4. The dye according to Claim 1 of the formula



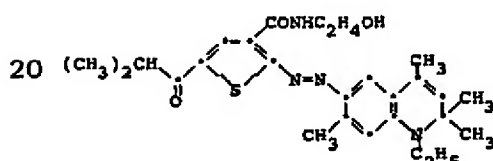
5. The dye according to Claim 1 of the formula



6. The dye according to Claim 1 of the formula

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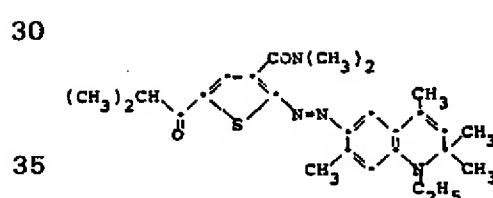
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7. The dye according to Claim 1 of the formula

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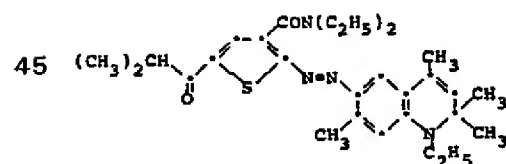
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8. The dye according to Claim 1 of the formula

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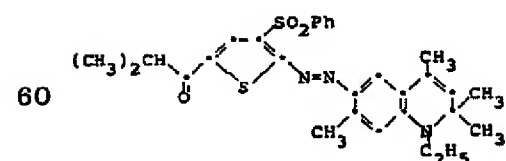
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9. The dye according to Claim 1 of the formula

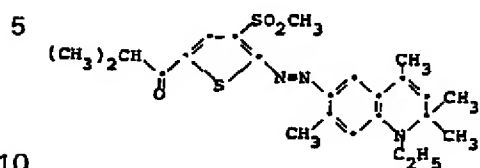
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10. The dye according to Claim 1 of the formula

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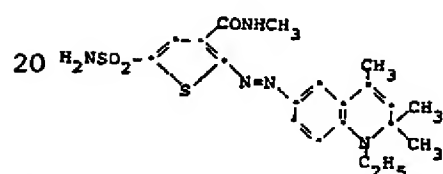
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11. The dye according to Claim 1 of the formula

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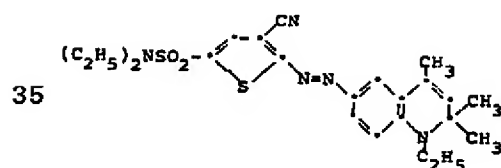
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12. The dye according to Claim 1 of the formula

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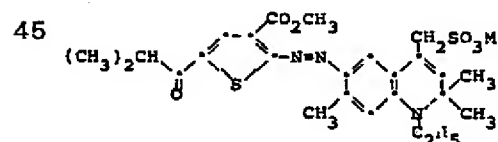
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13. The dye according to Claim 1 of the formula



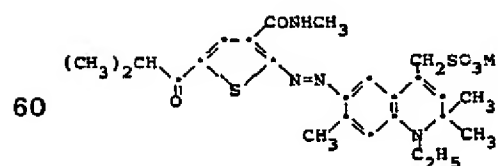
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14. The dye according to Claim 1 of the formula

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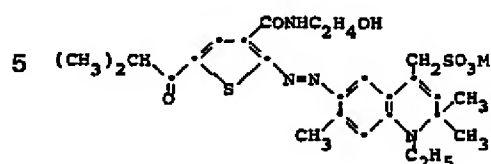
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15. The dye according to Claim 1 of the formula



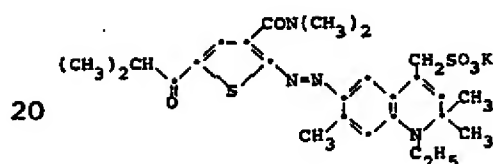
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16. The dye according to Claim 1 of the formula

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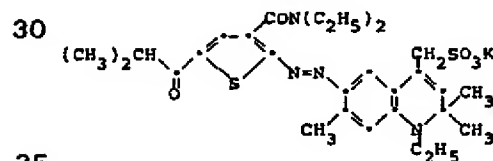
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17. The dye according to Claim 1 of the formula



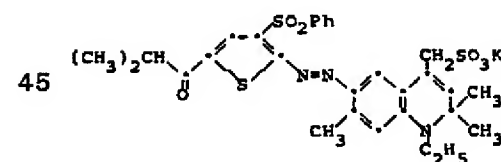
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18. The dye according to Claim 1 of the formula

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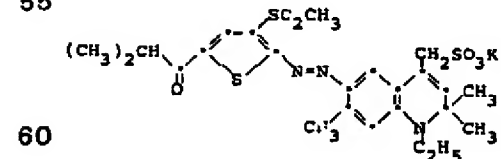
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19. The dye according to Claim 1 of the formula

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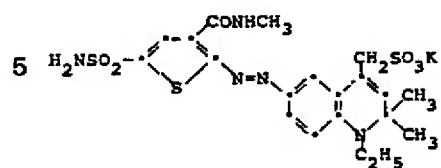
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20. The dye according to Claim 1 of the formula



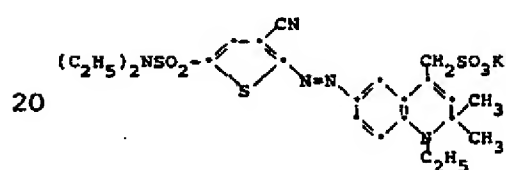
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21. The dye according to Claim 1 of the formula

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Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1985, 4235.
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